

~~RESTRICTED DATA~~  
ATOMIC ENERGY ACT OF 1954

~~CONFIDENTIAL~~

~~CONFIDENTIAL RESTRICTED DATA~~  
NASA TECHNICAL  
MEMORANDUM



NASA TM X-1059

NASA TM X-1059

CLASSIFICATION GROUP 1

TO ~~CONFIDENTIAL~~  
UNCLASSIFIED

By authority of E.O. No. 13526  
*changed by* *4/23/13*

FUEL-RETENTION PROPERTIES  
OF TUNGSTEN — URANIUM  
DIOXIDE COMPOSITES (U)

*by Michael A. Gedwill, Paul F. Sikora,  
and Robert M. Caves*

*Lewis Research Center  
Cleveland, Ohio*

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • FEBRUARY 1965

~~CONFIDENTIAL RESTRICTED DATA~~

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~  
~~CONFIDENTIAL~~

NASA TM X-1059

065-1477

**CLASSIFICATION CHANGE**  
TO ☒ **UNCLASSIFIED**  
By authority of T.D. No. 73-327  
Changed by O.L. Meritt Date 4/25/73

FUEL-RETENTION PROPERTIES OF TUNGSTEN -  
URANIUM DIOXIDE COMPOSITES

By Michael A. Gedwill, Paul F. Sikora,  
and Robert M. Caves

Lewis Research Center  
Cleveland, Ohio

~~RESTRICTED DATA~~  
~~CONFIDENTIAL~~  
~~CONFIDENTIAL~~

~~CLASSIFIED DOCUMENT - THIS DOCUMENT IS UNCLASSIFIED~~  
~~This material contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18, U.S.C., Secs. 793 and 794, the transmission or revelation of which in any manner to an unauthorized person is prohibited by law.~~

~~NOTICE~~  
~~This document should not be returned after it has satisfied your needs. It may be disposed of in accordance with security regulations or the applicable provisions of the Atomic Energy Act for Safe-Guarding Classified Information.~~

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

~~CONFIDENTIAL~~  
~~CONFIDENTIAL~~

065-1477

~~CONFIDENTIAL~~  
~~RESTRICTED DATA~~  
FUEL-RETENTION PROPERTIES OF TUNGSTEN -

URANIUM DIOXIDE COMPOSITES\*

by Michael A. Gedwill, Paul F. Sikora  
and Robert M. Caves

Lewis Research Center

50299  
SUMMARY

Although tungsten - uranium dioxide composites appear very promising, as fuel element materials for high-temperature nuclear rocket reactors, one of the major problems with these materials is the loss of fuel at reactor operating temperatures (near or above 4500° F). Substantial fuel losses occur by vaporization whenever the uranium dioxide is directly exposed to elevated temperature environments and by fuel migration and vaporization when reactor operating conditions that involve thermal cycling are simulated. Several methods of minimizing fuel loss have been evaluated and appear quite promising.

Fuel loss from tungsten - uranium dioxide composites involves one or more of the following mechanisms:

- (1) Loss by vaporization of exposed and interconnected fuel particles
- (2) Thermal decomposition of fuel and subsequent migration of products
- (3) Diffusion of fuel through micropores and/or microcracks
- (4) High vapor pressures exerted by impurities present in composites
- (5) Differences in thermal expansivities of tungsten and uranium dioxide
- (6) Interaction of fuel with a reactive atmosphere such as hydrogen

The approaches being studied to minimize or inhibit fuel loss are

- (1) Complete surface cladding of composites with unfueled tungsten
- (2) Tungsten coating of uranium dioxide particles prior to consolidation
- (3) Use of fine fuel particles
- (4) Addition of small amounts of fine thoria particles to tungsten matrix.

Conf. R. 15 -

~~CONFIDENTIAL~~  
Unclassified.

Author  
~~RESTRICTED DATA~~

~~CONFIDENTIAL~~

## INTRODUCTION

Dispersions of uranium dioxide ( $\text{UO}_2$ ) in tungsten (W) are being considered as the fuel element material in a nuclear rocket reactor concept currently being studied at the NASA Lewis Research Center. This concept (described in ref. 1) requires that the W- $\text{UO}_2$  fuel elements (containing 10 to 30 volume percent fuel) operate in a rapidly flowing hydrogen atmosphere at temperatures as high as  $4500^\circ\text{F}$  for intermittent periods totaling up to 10 hours at maximum temperature. Studies are being conducted at the Lewis Research Center to define and seek solutions to potential materials problems of this reactor concept and to establish the operating limits for the potential fuel element materials. Results of initial studies of these materials in the areas of fabrication, property evaluation, fuel retention, and compatibility have been previously reported (ref. 2). The results of more recent fabrication and property evaluation studies are reported in reference 3, and this report describes the results of concurrent studies in the areas of fuel retention and fuel-matrix compatibility.

The problem of fuel retention in the W- $\text{UO}_2$  system stems primarily from the inherent high vapor pressure of  $\text{UO}_2$  at elevated temperatures (ref. 4). This high vapor pressure results in rapid volatilization of all fuel that is exposed to the operating atmosphere at temperatures of interest for nuclear rocket applications. Several potential methods of minimizing this surface vaporization are being studied, and the results appear quite promising. These studies, however, have indicated that the fuel containment problem can be compounded by several other interrelated factors. Therefore, detailed investigations are being conducted to evaluate the effects of these factors and to determine methods of overcoming or controlling them. The current results from these studies are described in this report.

## MATERIALS

For most of the studies described in this report, rectangular-plate samples containing 80 volume percent tungsten and 20 volume percent uranium dioxide (80W + 20 $\text{UO}_2$ ) were used. These samples were fabricated by the powder-metallurgy process described in reference 3. This process involves the pressing and sintering of powder composites followed by hot rolling to produce dense plates (greater than 98 percent of theoretical density). The characteristics of the starting materials of these composites were as follows:

### Uranium dioxide

Purity, percent . . . . .	99.9
Firing temperature, $^\circ\text{F}$ . . . . .	3100
Oxygen-uranium ratio . . . . .	$2.005 \pm 0.005$
Average diameter of spherical particles, microns . . . . .	50

### Tungsten

Purity, percent . . . . .	99.9
Average particle size, microns . . . . .	0.88

The impurities in the starting materials are included in table I as an indication of the purity levels present in the W- $\text{UO}_2$  composites because accu-



CONFIDENTIAL RESTRICTED DATA

TABLE I. - CHEMICAL ANALYSES OF STARTING  
URANIUM DIOXIDE AND TUNGSTEN POWDERS

Element	Uranium dioxide, <sup>a</sup> parts per million by weight	Tungsten, parts per million by weight	Element	Uranium dioxide, <sup>a</sup> parts per million by weight	Tungsten, parts per million by weight
Aluminum	160	<2	Lead	<0.01	<0.01
Beryllium	<0.1	<0.1	Magnesium	0.1	0.2
Boron	<0.1	<0.1	Manganese	3	<0.1
Cadmium	<0.01	<0.01	Molybdenum	50	3
Calcium	1	1	Nickel	1	1
Carbon	25	30	Nitrogen	16	----
Chromium	0.8	0.5	Silicon	<50	3
Cobalt	<5	<0.01	Tin	<0.01	<0.01
Copper	0.2	0.05	Titanium	0.2	<0.1
Fluorine	<0.1	<0.1	Vanadium	0.05	0.08
Iron	12	6	Zirconium	75	----

<sup>a</sup>88.09 weight percent uranium; ratio of oxygen to uranium atoms, 2.005±0.005.

rate methods of analyzing for trace impurities in W-UO<sub>2</sub> composites are not currently available.

#### APPARATUS AND TEST PROCEDURES

High-temperature fuel-retention tests were conducted in hydrogen, helium, or vacuum. All tests in hydrogen and helium atmospheres were conducted in a high-temperature induction furnace (described in ref. 5). Gas flow rates of 35 standard cubic feet per hour of hydrogen or 25 standard cubic feet per hour of helium were employed during these tests. Tank-grade (99.9-percent minimum purity) hydrogen and helium gases were used, but these were purified before being supplied to the furnace. A combination of two liquid-nitrogen cold traps and a commercial palladium catalyst precombiner were used to purify the hydrogen gas. Helium gas was purified by being passed through a train consisting of two liquid-nitrogen cold traps and zirconium chips, which were heated at 1600° F. Although impurities in the purified gases were not analyzed, it is believed that the oxygen, hydrocarbon, and moisture contents of the gases entering the furnace were each less than 1 part per million by volume. For a test temperature of 4500° F in either a hydrogen or a helium atmosphere, the samples were heated and cooled in about 10 minutes.

All vacuum tests were conducted at a total pressure of about  $3 \times 10^{-5}$  torr in a vacuum furnace, which used tungsten resistance heating elements. In this furnace, test samples were heated and cooled in 15 and 45 minutes, respectively, for a test temperature of 4500° F.

During the operation of these furnaces, temperature measurements were made by sighting a micropyrometer onto a blackbody hole in a tungsten block,

which was placed in the furnace adjacent to the test samples. The estimated accuracy of the temperature measurements was  $\pm 30^{\circ}$  F at  $4500^{\circ}$  F.

In order to obtain precise measurements of fuel losses resulting from treatments at high temperatures ( $\geq 3500^{\circ}$  F), it was deemed necessary to treat each test sample prior to testing in order to remove any spurious surface contaminants. Thus, each sample was ultrasonically cleaned in laboratory-grade ethyl alcohol for several minutes and then given a preliminary bakeout for 1/2 hour in hydrogen at  $3000^{\circ}$  F. The fuel loss determinations involved weight measurements to within 0.1 milligram before and after the high-temperature treatments. The resultant weight losses for the test samples were assumed to be due only to  $\text{UO}_2$  losses because similarly tested, unfueled tungsten samples showed no measurable weight losses. In addition to fuel loss determinations, the test samples were also metallographically evaluated, and a few selected test samples were submitted for electron microprobe analyses.

## RESULTS AND DISCUSSION

### Factors Affecting Fuel Loss

Although surface vaporization at elevated temperatures is the prime mode

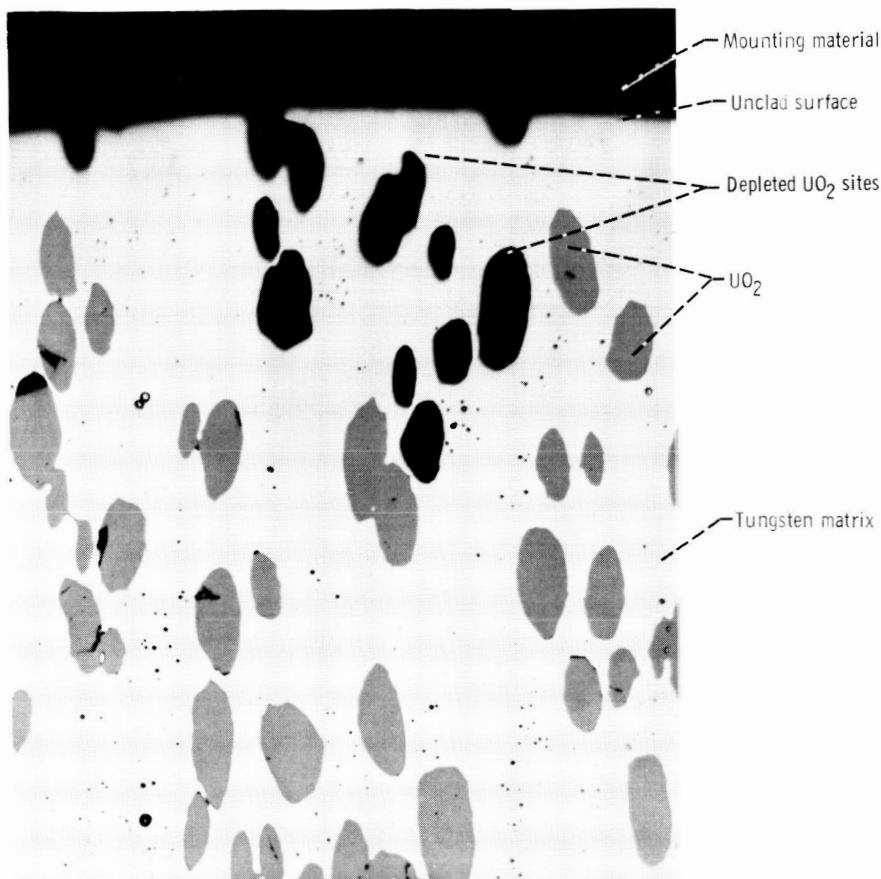


Figure 1. - Microstructure of heat-treated unclad 80-volume-percent-tungsten - 20-volume-percent-uranium dioxide sample. Unetched. X250.

of fuel loss from W-UO<sub>2</sub> composites, loss of fuel can be affected by several factors that are characteristic of the composites. Four effects that were observed in this investigation are discussed briefly in the following paragraphs.

Interconnection of fuel particles. - At elevated temperatures, serious fuel losses from W-UO<sub>2</sub> composites can result whenever interconnections exist between internal and exposed fuel particles. An example of this is shown in figure 1.

This sample was heat-treated at 4500° F for 10 hours in helium. The irregular pattern of the depleted fuel sites in figure 1 suggests that the UO<sub>2</sub> particles adjacent to the unclad surface of the sample vaporized off and were followed by the internal UO<sub>2</sub> particles that were interconnected with the exposed particles (in three dimensions).

Diffusion of fuel through micropores and microcracks. - The resulting vaporization of the fuel at the surfaces of W-UO<sub>2</sub> composites can occur by means of diffusion of the fuel through micropores and microcracks contained within the tungsten matrix. An example of this type of diffusion in 80W + 20UO<sub>2</sub> composites at elevated temperatures is shown in figure 2. These samples were

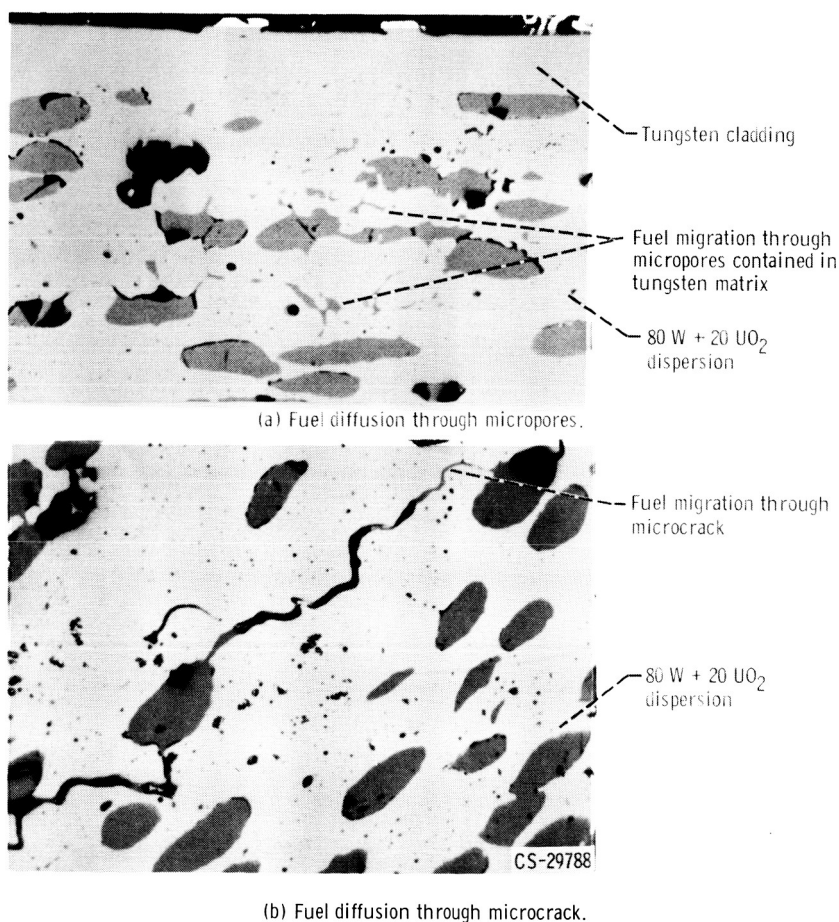
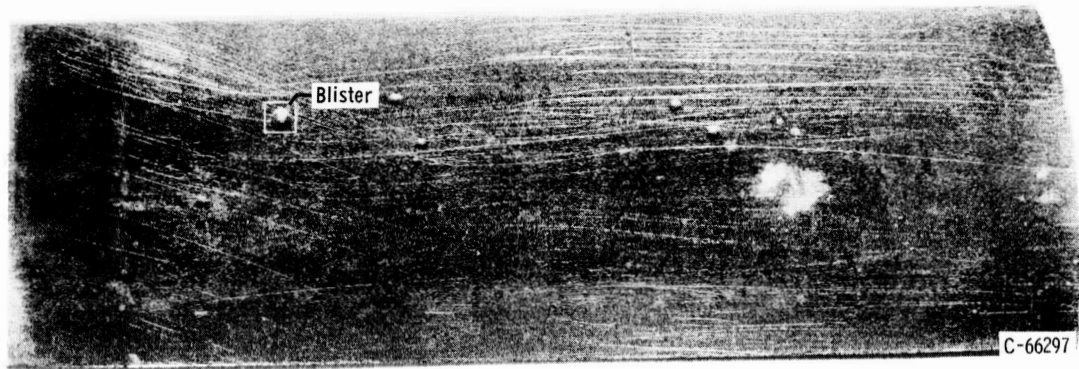


Figure 2. - Microstructures of two 80-volume-percent-tungsten - 20-volume-percent-uranium dioxide samples. Unetched. X300.

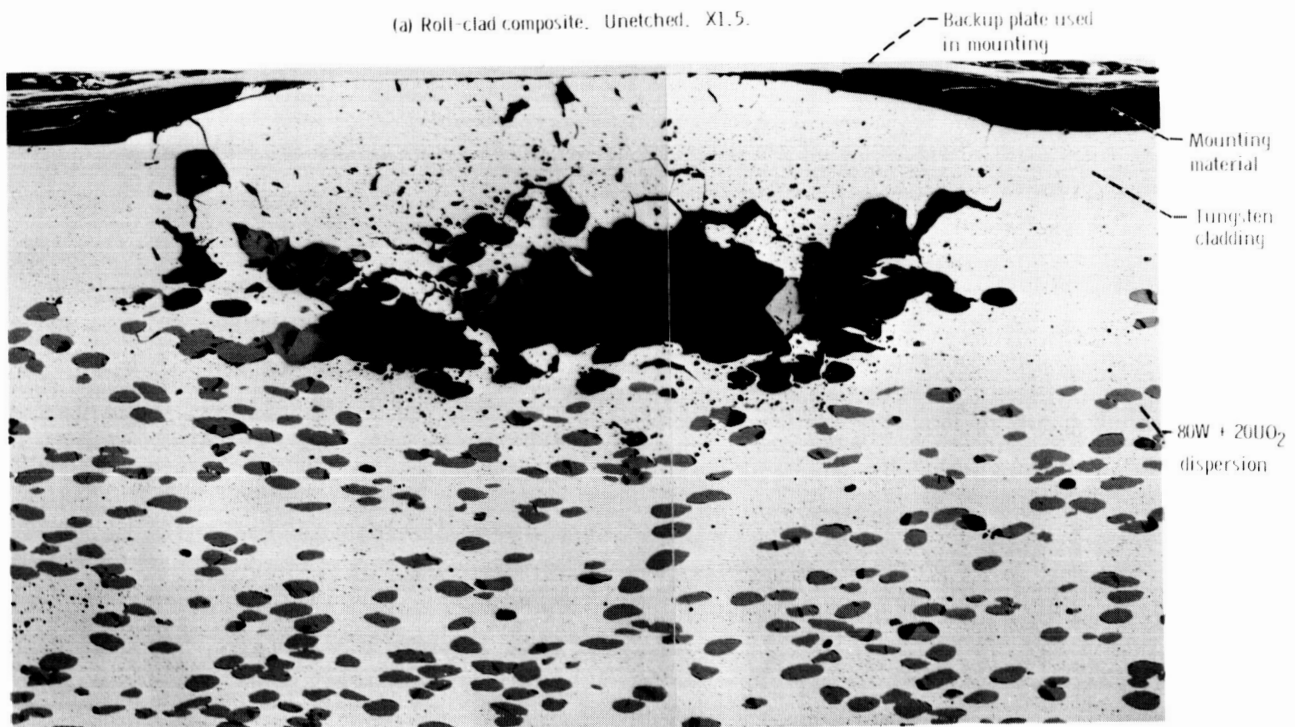
~~CONFIDENTIAL RESTRICTED DATA~~

heat-treated for a 2-hour period at 4500° F in hydrogen. Migration of the fuel through micropores and microcracks can occur by means of either solid- or vapor-phase transport or a combination of these.

High local concentrations of impurities. - Fuel loss by vaporization may be through surface faults that are caused by impurities being concentrated in localized regions within the composites. The high vapor pressures of these impurities at elevated temperatures can cause the clad to blister and eventually rupture. As an example, figure 3 shows a blistered region in a W-UO<sub>2</sub> composite that was subjected to a 2-hour heat treatment at 4500° F in hydrogen. The blister probably resulted from high internal pressures generated by impurities being concentrated in this region.



(a) Roll-clad composite. Unetched. X1.5.



(b) Cross section of blister shown in (a). Unetched. X100.

Figure 3. - Effect of impurities in heat-treated roll-clad 80-volume-percent-tungsten - 20-volume-percent uranium dioxide composite.

~~CONFIDENTIAL RESTRICTED DATA~~

Chemical analysis of the  $\text{UO}_2$  lot used for this sample revealed high concentrations of alumina ( $\text{Al}_2\text{O}_3$ ) and silica ( $\text{SiO}_2$ ), and it is believed that these impurities were the result of the methods employed in processing the  $\text{UO}_2$ . Thus, it is evident that extreme care must be exercised in all phases of material processing to preclude the pickup of such impurities.

Partial decomposition of the fuel. - Although vaporization is the predominant mechanism by which fuel is lost, decomposition of  $\text{UO}_2$  can occur thermally (ref. 6) and at an accelerated rate in the presence of a reactive atmosphere, such as hydrogen. Chemical interaction between hydrogen and  $\text{UO}_2$  (per se or its decomposition products) results in the formation of a uranium-rich phase, as shown in figure 4. The  $80\text{W} + 20\text{UO}_2$  sample shown in figure 4 was heat-treated for a 10-hour period at  $4500^\circ\text{F}$  in hydrogen. Electron-microprobe analyses of samples of this type indicated that the minute white particles dispersed in the  $\text{UO}_2$  are rich in uranium, and they are thought to be metallic uranium. Similar particles in the  $\text{UO}_2$  dispersoids of samples that were heat-treated at  $4500^\circ\text{F}$  in vacuum and in inert-gas atmospheres were also observed but in lesser quantities. Subsequent metallographic evaluations and electron-microprobe analyses revealed that these particles were also rich in uranium.

#### Studies of Methods to Improve Fuel Containment

Surface claddings. - In order to minimize the loss of fuel at elevated temperatures, two approaches are being studied at the Lewis Research Center. One of these involves the addition of a thin layer of tungsten completely encapsulating the fueled composite. In essence, this external cladding should prevent loss of surface  $\text{UO}_2$  particles and, similarly, all internal  $\text{UO}_2$  particles.

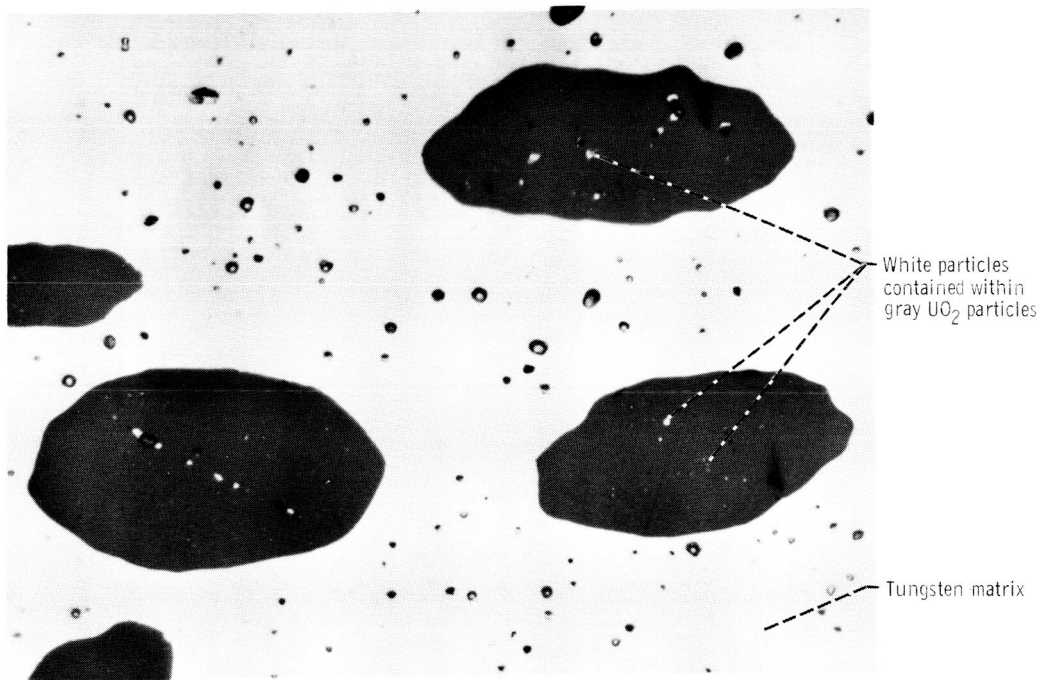


Figure 4. - Effect of partial decomposition of uranium dioxide particles in tungsten matrix. Unetched. X1000.

~~CONFIDENTIAL RESTRICTED DATA~~

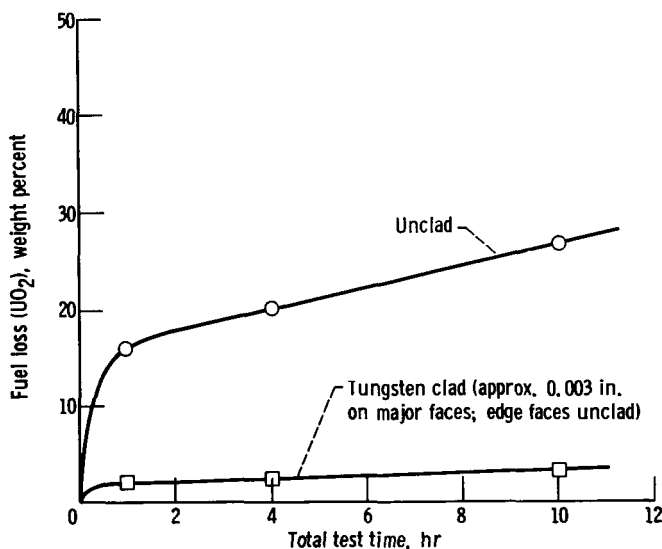


Figure 5. - Effect of cladding on fuel loss from 80-volume-percent-tungsten - 20-volume-percent-uranium dioxide samples. Test temperature, 4500° F; vacuum ( $3 \times 10^{-5}$  torr); sample size, 5/8 by 5/8 by 0.03 inch.

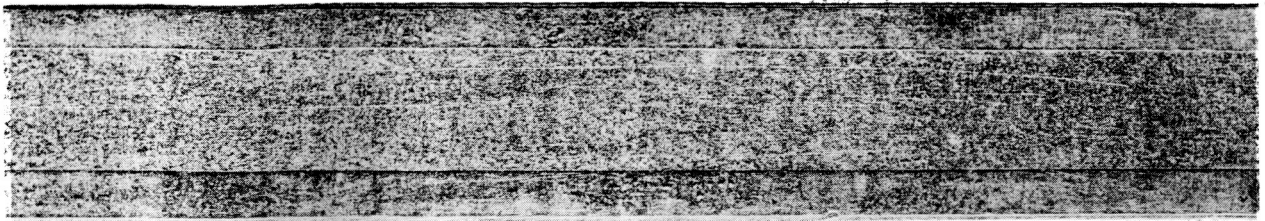
The validity of this approach was tested by vacuum annealing two series of similarly fabricated 80W + 20UO<sub>2</sub> plate samples at 4500° F. One series of the samples was unclad; the other series of samples was clad on the two major faces with tungsten foil approximately 3 mills thick, but the edges remained unclad. The cladding on these samples was applied by the roll-bonding process described in reference 3. Fuel losses of these two series of samples were measured and are plotted as a function of time at temperature in figure 5. This plot shows that the unclad samples lost a considerable amount of their fuel, whereas the face-clad samples lost very little, that is, 27 weight percent against about 3 weight percent in 10 hours, respectively. Subsequent metallographic examination of the cross sections of the face-clad samples indicated that nearly all loss of fuel was through the unclad edges. This is assumed to be the loss of the exposed and interconnected particles at the edges. Since face claddings can be easily applied during the rolling of flat-plate specimens, claddings of this type were used on many of the test specimens described in later portions of this report.

In view of these encouraging results, several different methods of applying external tungsten claddings to all surfaces of W-UO<sub>2</sub> composites are currently being evaluated and are briefly discussed in the following paragraphs.

Gas-pressure bonding: Tungsten foil (0.001 in. thick) has been clad on all surfaces of 80W + 20UO<sub>2</sub> composites by the gas-pressure bonding process described in reference 7, and results of subsequent fuel-loss tests have indicated that cladding applied in this manner offers an effective method of fuel containment. Essentially no measurable fuel losses have been observed for pressure-bonded 80W + 20UO<sub>2</sub> composites when continuously heat-treated at 4500° F for a 2-hour period in either vacuum or hydrogen. A pressure-bonded W-UO<sub>2</sub> composite that was heat-treated is shown in figure 6.

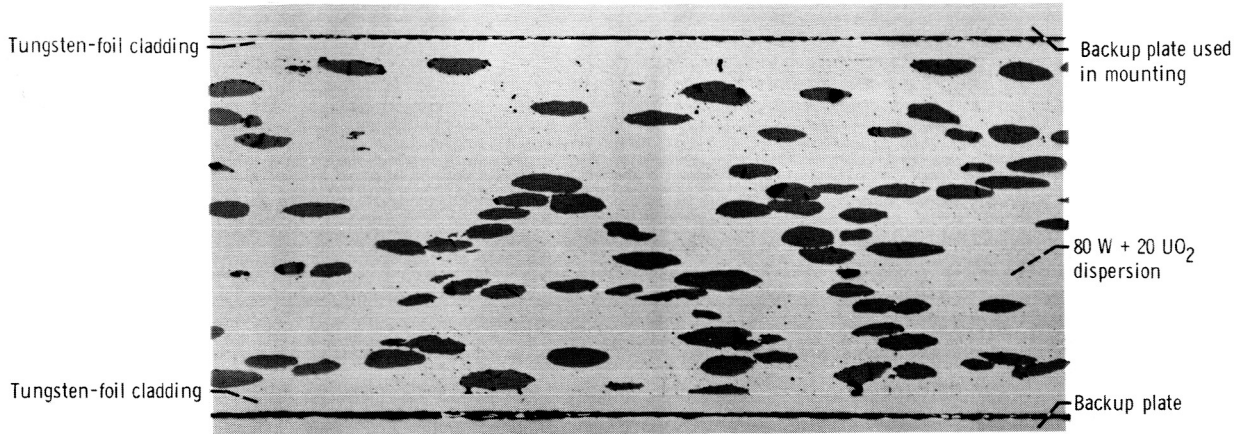
~~CONFIDENTIAL RESTRICTED DATA~~





(a) Pressure-bonded composite. Unetched. X1.5.

C-66493



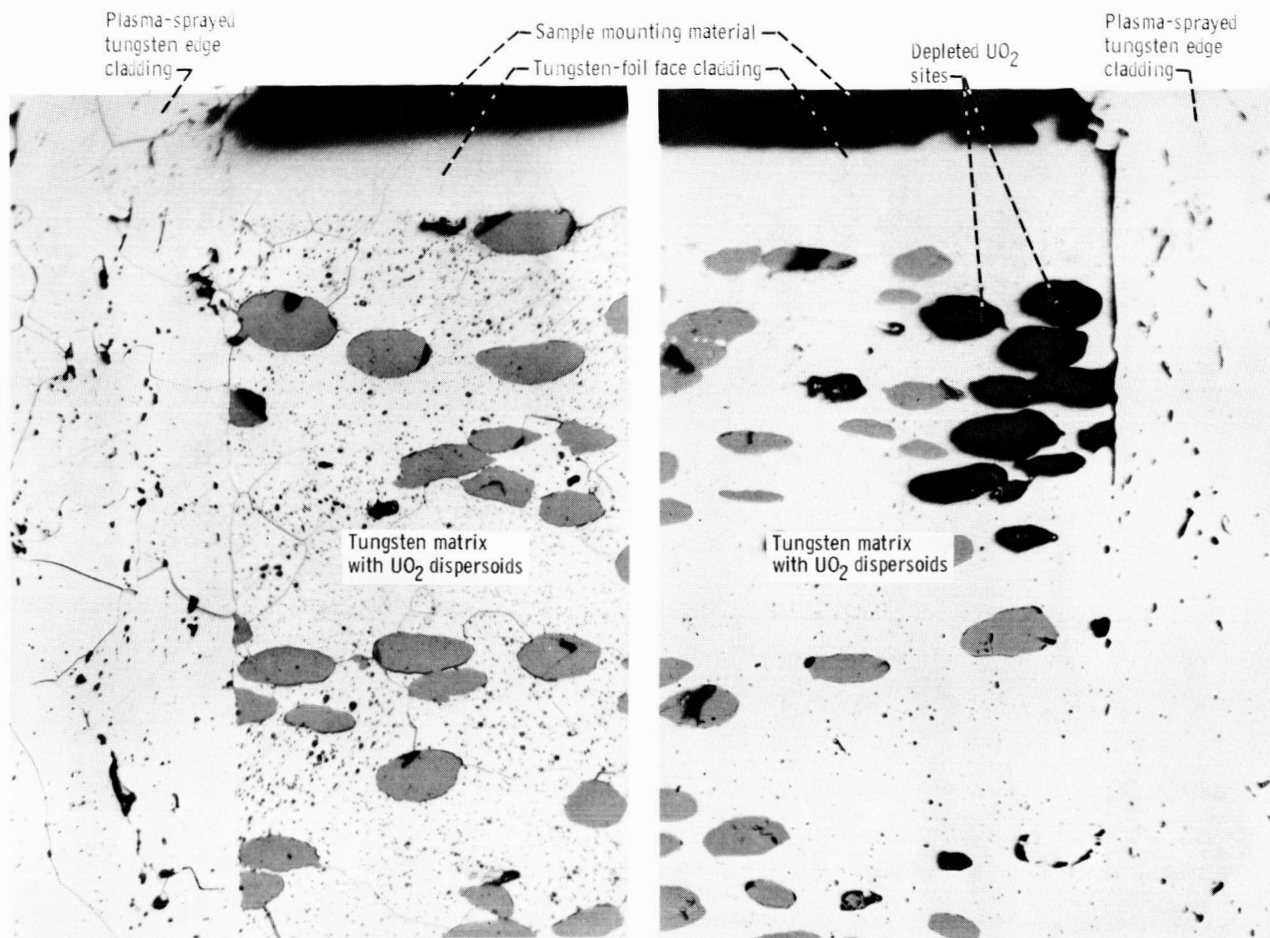
(b) Microstructure of longitudinal section of composite shown in (a). Unetched. X100.

Figure 6. - Pressure-bonded 80-volume-percent-tungsten - 20-volume-percent-uranium dioxide composite. Heat-treated at 4500° F in hydrogen for 2 hours.

**Vapor deposition:** Several W-UO<sub>2</sub> composites have been completely surface clad by vapor deposition techniques (as described in ref. 8). A limited number of vapor-clad composites have been evaluated to date, and the majority have not been successful in retaining the fuel. The vapor-clad composites showing the most promise were coated by the hydrogen reduction of either tungsten fluoride or tungsten chlorides. Major faults with this type of clad W-UO<sub>2</sub> composite have been spalling and blistering of the cladding during tests in hydrogen at 4500° F. This blistering appears to be due to incomplete metallurgical bonding and to occlusion of impurities, probably both hydrogen and halides, during the coating process. Therefore, cladding by this method needs considerably more study before it can be considered for reactor use.

**Plasma spraying:** Preliminary results (ref. 5) of the use of plasma-sprayed tungsten as edge cladding for face-clad W-UO<sub>2</sub> composites have been highly encouraging from a fuel retention standpoint. At temperatures up to 4500° F in either hydrogen or vacuum, no appreciable fuel loss (less than 1 weight percent) was observed from these samples when complete bonding had been achieved prior to the elevated temperature treatment, as shown in figure 7(a). When the bonding is incomplete, however, fuel is lost through the defective area (fig. 7(b)). This process of cladding may be particularly useful as a method of sealing defects in claddings produced by other processes.

**Tungsten-coated fuel particles.** - Tungsten coating of uranium dioxide particles is the alternative approach being studied as a means of optimizing



(a) Edge cladding completely bonded. Etched (Murakami's reagent).

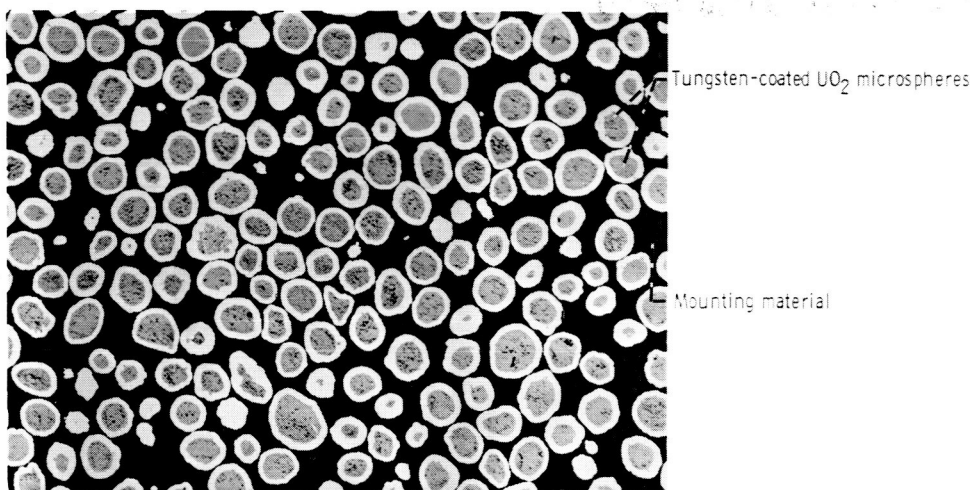
(b) Edge cladding not completely bonded. Unetched.

Figure 7. - Plasma-sprayed, tungsten-edge-clad 80-volume-percent-tungsten - 20-volume-percent-uranium dioxide composites. X250.

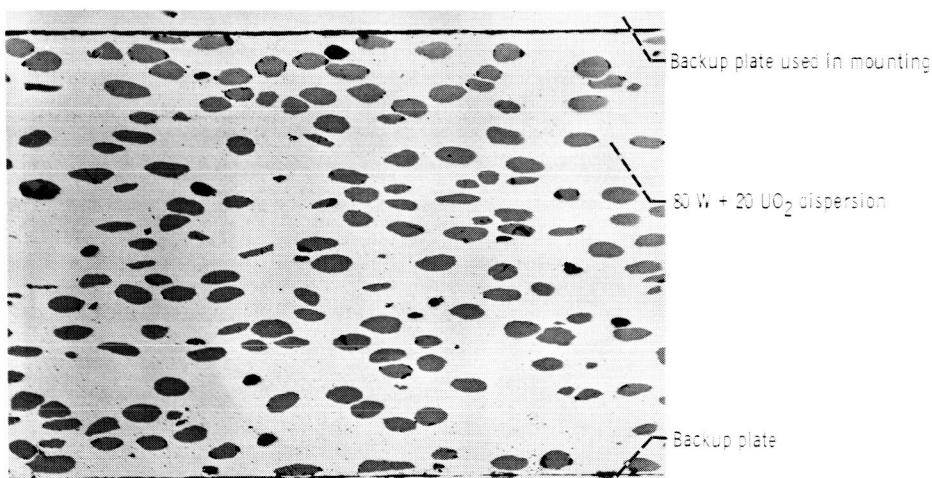
fuel retention. This "inner-cladding" method involves the use of coated particles to produce dense composites, which may or may not require an external cladding. This method offers the prime advantages of uniform particle spacing and complete separation of the fuel particles.

Limited quantities of tungsten-coated UO<sub>2</sub> particles have been received to date. An example of some coated particles is shown in figure 8(a). These UO<sub>2</sub> particles, which were prepared by hydrogen reduction of tungsten flouride in a fluidized bed and are about 50 microns in diameter, are coated with a tungsten layer about 12 microns thick. Coated particles similar to these were consolidated into dense plates by the fabrication technique described in reference 3. A cross section of one of these plates is shown in figure 8(b). A sample taken from this plate was subjected to a 2-hour heat treatment at 4500° F in hydrogen. The effect of this heat treatment on the microstructure is shown in figure 8(c). Only a few UO<sub>2</sub> particles located near the surface of the sample were lost through vaporization, but essentially none of the internal

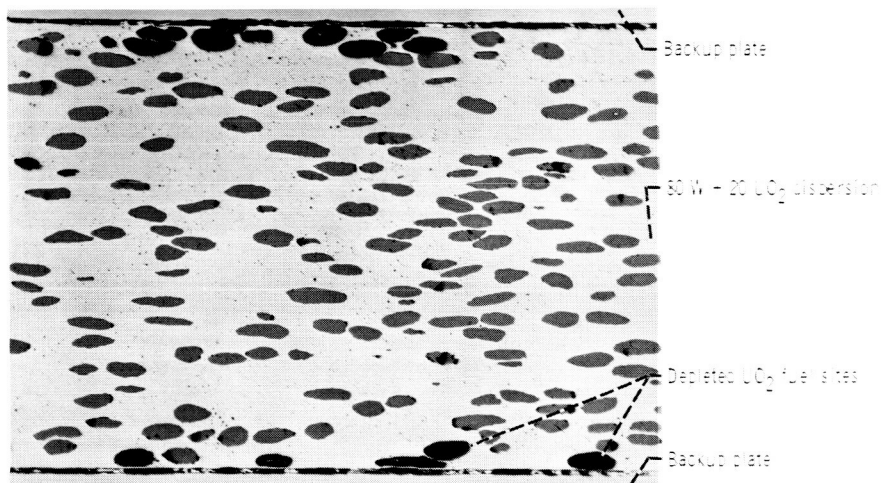




(a) Tungsten-coated uranium dioxide microspheres.



(b) Plate fabricated from tungsten-coated uranium dioxide microspheres.



(c) Heat-treated 80-volume-percent-tungsten - 20-volume-percent-uranium dioxide sample that was fabricated from tungsten-coated uranium dioxide microspheres. Unetched. X100.

Figure 8. - Tungsten-coated uranium dioxide. (Reduced 22 percent in printing.)

~~CONFIDENTIAL RESTRICTED DATA~~

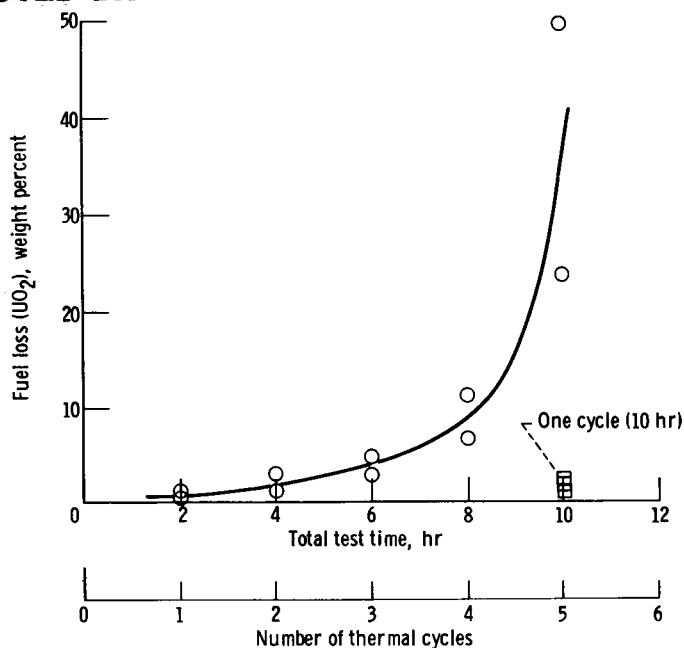


Figure 9. - Effect of thermal cycling on fuel losses from roll-clad 80-volume-percent-tungsten - 20-volume-percent-uranium dioxide samples. Samples were subjected to subsequent heat treatments at 2-hour intervals at 4500° F in hydrogen (35 standard cu ft/hr) with intermittent cooling to ambient temperatures. Sample size,  $1\frac{3}{8}$  by 0.028 inch (approx. 0.002 in. tungsten clad on major faces); uranium dioxide particle diameter, 30 to 60 microns.

UO<sub>2</sub> particles were lost. Thus, precoating of the fuel particles appears to be an effective method of reducing fuel vaporization losses.

Although these results demonstrate the promise of the inner cladding method, it is believed that high fluorine contents in coated particles produced by fluoride-reduction methods can be detrimental to fuel retention at elevated temperatures because of the high volatility of entrapped uranium fluorides. Chemical analyses of several batches of UO<sub>2</sub> particles coated by hydrogen reduction of tungsten fluoride have shown fluorine contents in the range 300 to 3000 parts per million by weight. At present, several programs are in progress that call for the preparation of high-purity coated particles by various processes as well as for the consolidation of these particles into dense bodies.

#### Studies of Effects of Thermal Cycling

Until very recently, the fuel retention results of the cladding studies looked very encouraging, and it appeared that fuel containment in W-UO<sub>2</sub> composites at elevated temperatures would not be as difficult a problem as originally envisioned. Recent results, however, have indicated that the fuel containment problem is greatly amplified by thermal cycling. This first became apparent when several roll-clad W-UO<sub>2</sub> samples (edges unclad) were subjected to

~~CONFIDENTIAL RESTRICTED DATA~~

a series of five subsequent 2-hour heat treatments at 4500° F in hydrogen with intermittent cooling to ambient temperatures. The results of this initial thermal cycling experiment are summarized in figure 9, which shows fuel losses plotted against the total time at 4500° F and the corresponding number of thermal cycles from ambient temperatures. Each circle represents the fuel loss from cycling a particular sample to 4500° F in hydrogen. The first two cycles produced very little fuel loss, but subsequent cycles resulted in a rapid acceleration of the fuel loss. The adverse effect of thermal cycling is readily apparent in figure 9 when the total fuel loss from the thermally cycled samples is compared with that from any of three samples that were heated in hydrogen for the same total time, that is, for 10 hours but with no intermediate cycling. The rapid increase in fuel loss from these samples is shown in the photomicrographs of figure 10. These photomicrographs were taken from the cross sections of the samples that were heat-treated in hydrogen for one, three, and five 2-hour intervals and for which the fuel loss data are shown in figure 9. Although the photomicrographs of low magnification (X100) indicate an apparent intergranular cracking of both the tungsten matrix and cladding as a result of increased thermal cycling, it becomes apparent when viewed at higher magnification (X500) that this cracking is actually migration of fuel through the tungsten grain boundaries. This migration results in a weakening of the tungsten matrix and the eventual breakup of the clad sample. The weak bonds between the grains led to the result shown in figure 10(c); that is, several of the tungsten grains were pulled out during metallographic preparation. Metallographic examination of the samples that were heat-treated for one 2-hour and one 10-hour interval in hydrogen (figs. 10(a) and (d), respectively) shows that their structures were essentially the same and indicates that the loss of fuel occurred only where fuel particles were exposed and interconnected at the unclad edges; the time at temperature had little effect on the fuel loss. Fuel migration through the grain boundaries of the tungsten matrix was first evident in the samples after the second thermal cycle.

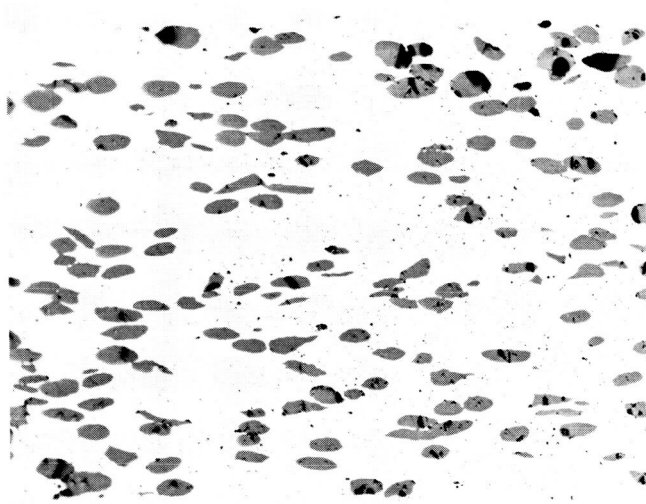
To determine the effects of thermal cycling on fuel containment and to seek methods of preventing or minimizing it, the following variables are being investigated:

Heat-treating variables

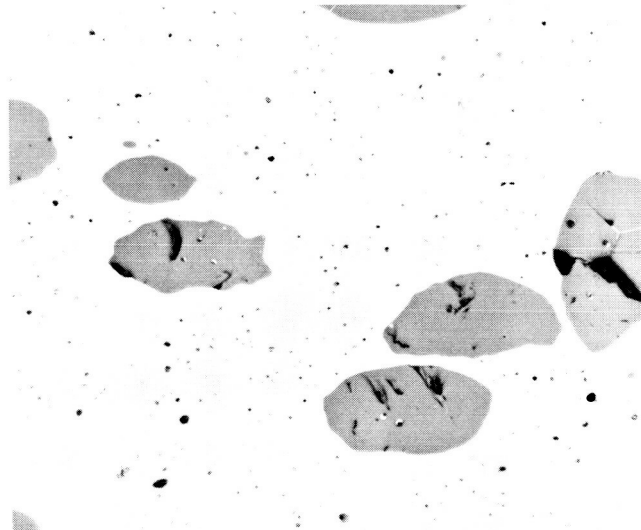
- (1) Number of thermal cycles
- (2) Time at Temperature - per cycle and cumulative
- (3) Atmosphere
- (4) Incubation period - variation in time at temperature during initial cycle
- (5) Temperature
- (6) Heating and cooling rates

Sample variables

- (1) Fuel particle size
- (2) Fuel stoichiometry
- (3) Purity of starting materials
- (4) Stabilizing additives

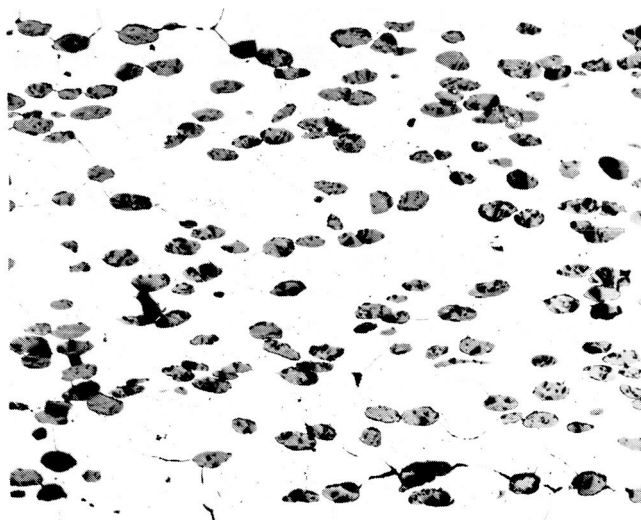


X100



X500

(a) One 2-hour cycle.



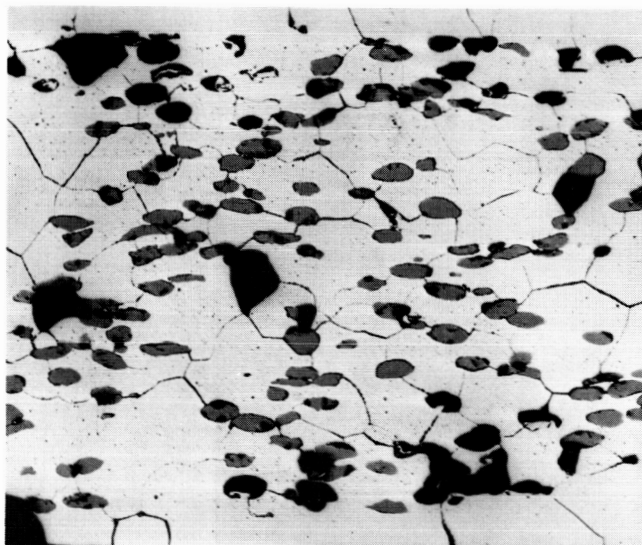
X100



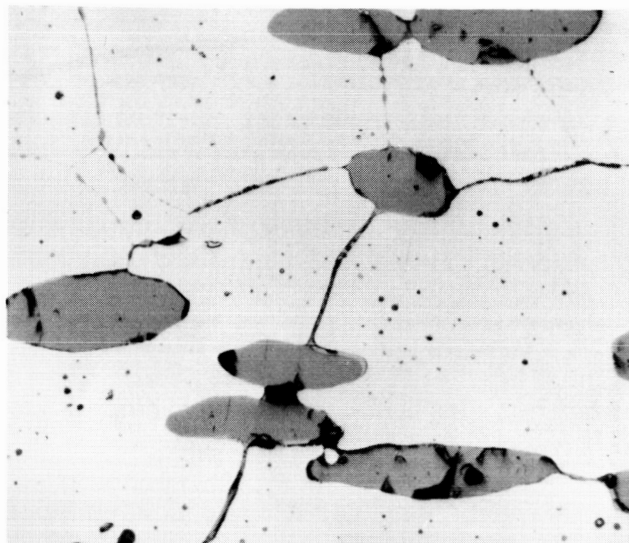
X500

(b) Three 2-hour cycles.

Figure 10. - Microstructures of thermally cycled, roll-clad 80-volume-percent-tungsten - 20-volume-percent uranium dioxide samples. Samples heat-treated at 4500° F in hydrogen with intermittent cooling to ambient temperatures. Unetched.

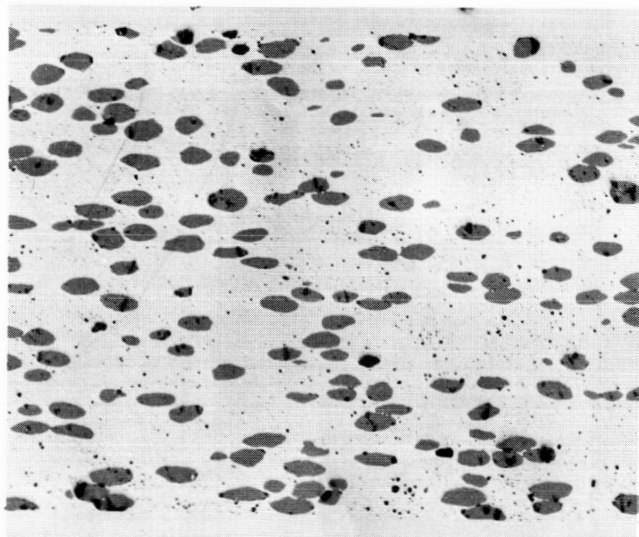


X100

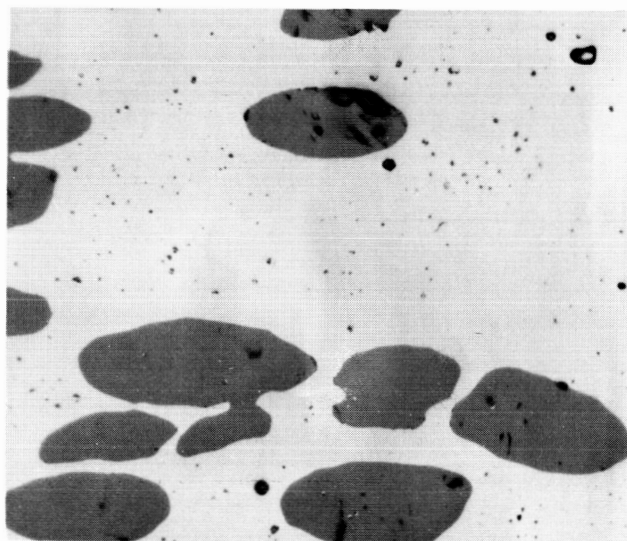


X500

(c) Five 2-hour cycles.



X100



X500

(d) One 10-hour cycle.

Figure 10. - Concluded. Microstructures of thermally cycled, roll-clad 80-volume-percent-tungsten - 20-volume-percent uranium dioxide samples. Samples heat-treated at 4500° F in hydrogen with intermittent cooling to ambient temperatures. Unetched.

From the results obtained to date, several tentative conclusions have been reached and are discussed in the following paragraphs.

In the study of the number of thermal cycles and the time at temperature, three similar series of roll-clad W-UO<sub>2</sub> samples were subjected to subsequent thermal cycles with holding times of 10 minutes, 1 hour, or 2 hours at 4500° F in hydrogen. The resultant fuel losses from these samples are plotted as a function of the total time at the test temperature in figure 11. As an example, the total fuel loss resulting from twelve 10-minute cycles (total of 2 hr at temperature) was about 18 weight percent, whereas six 1-hour cycles (total of

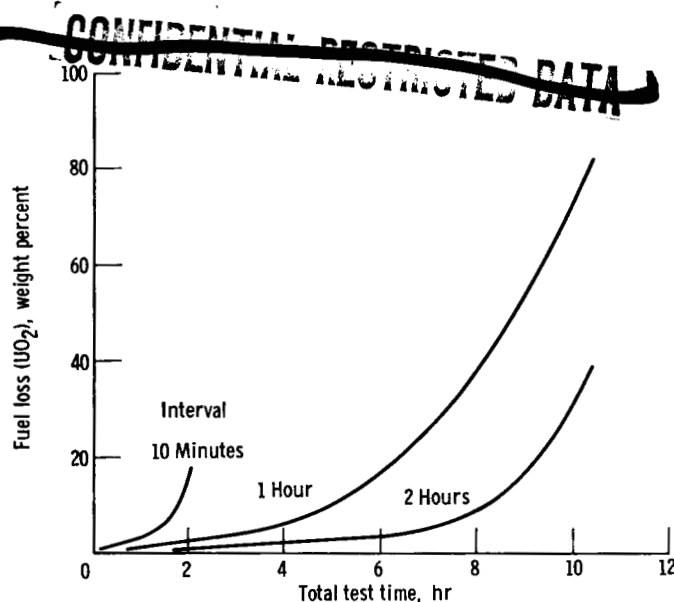


Figure 11. - Effect of time at temperature in thermal cycling roll-clad 80-volume-percent-tungsten - 20-volume-percent uranium dioxide samples. Samples were subjected to subsequent heat treatments at 4500° F in hydrogen (35 standard cu ft/hr) with intermittent cooling to ambient temperatures. Sample size,  $1\frac{3}{8}$  by 1 by 0.028 inch (approx. 0.002 in. tungsten clad on major faces); particle diameter, 30 to 60 microns.

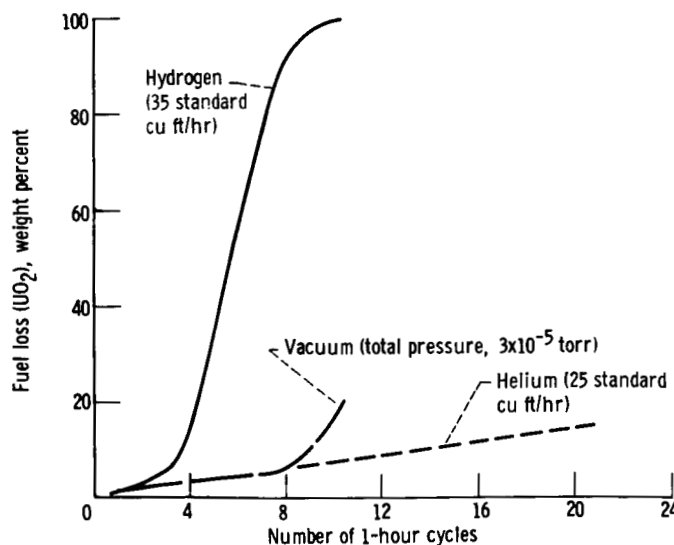


Figure 12. - Effect of test atmosphere in thermal cycling roll-clad 80-volume-percent-tungsten - 20-volume-percent-uranium dioxide samples. The samples were subjected to subsequent heat treatments at 1-hour intervals at 4500° F in hydrogen, vacuum, or helium with intermittent cooling to ambient temperatures. Sample size,  $1\frac{3}{8}$  by 1 by 0.021 inch (approx. 0.002 in. tungsten clad on major faces); particle diameter, 30 to 60 microns.

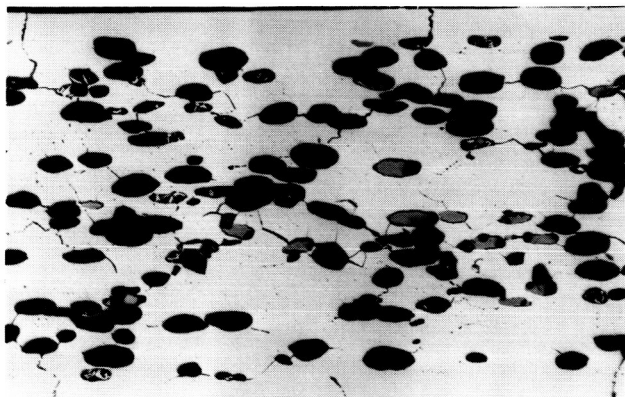
6 hr at temperature) were required for loss of the same amount of fuel. This again demonstrates that the number of thermal cycles has a more pronounced effect in producing the initial fuel loss or migration than does the total time at temperature.

Test atmosphere has also been studied. Three similar series of roll-clad W-UO<sub>2</sub> samples were thermally cycled in hydrogen, vacuum, or helium atmospheres. The resultant fuel losses from these samples are plotted in figure 12 as a function of the number of 1-hour cycles at 4500° F. Obviously, thermal cycling in hydrogen can result in catastrophic losses of fuel from samples after only three or four 1-hour cycles at 4500° F. Likewise, thermal cycling in vacuum has an effect on fuel loss, after nine cycles, but thermal cycling in helium has no appreciable effect on fuel loss since the resulting fuel-loss rate is constant. In all the samples cycled in helium, metallographic examinations showed that loss of fuel was through the unclad edges. Photomicrographs taken from selected samples that were cycled in hydrogen, helium, and vacuum are shown in figure 13. The photomicrographs of figure 13(a) show the catastrophic effect of cycling in hydrogen. Note in particular the following: (1) fuel migration is evident throughout the tungsten grain boundaries of both the matrix and the cladding, and (2) there is evidence of an additional phase at the W-UO<sub>2</sub> interfaces. (Electron microprobe analysis and metallographic evaluations showed this other phase to be rich in uranium.) The photomicrographs in figure 13(b) indicate that, after 15 thermal cycles in helium,

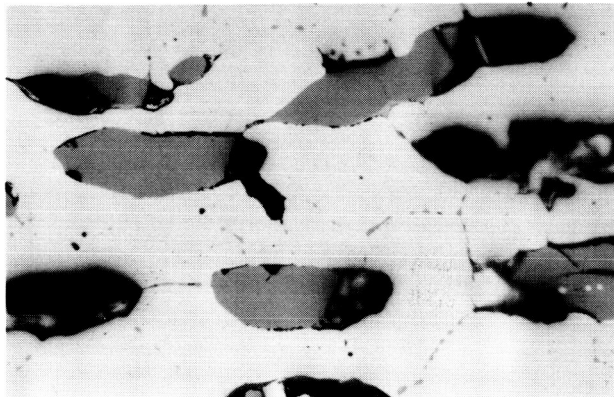


slight fuel migration is evident only in the tungsten matrix and is probably not sufficient to affect the overall behavior of this composite seriously. The photomicrographs of figure 13(c) show that, after eight thermal cycles in vacuum, fuel migration is only slightly evident in the tungsten cladding.

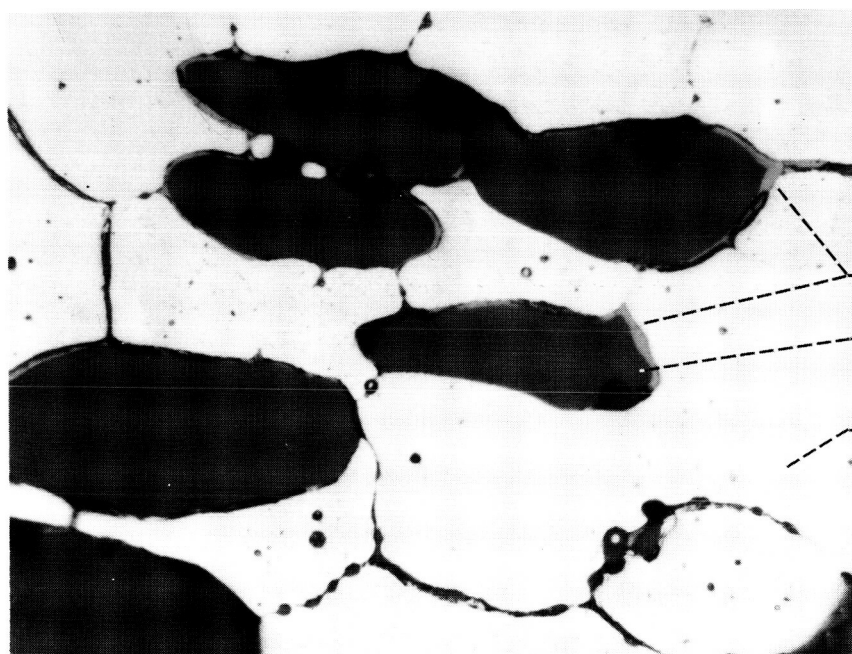
It is believed that this fuel containment problem is due to a thermal decomposition of  $\text{UO}_2$  at elevated temperatures and the subsequent loss of oxygen atoms from the  $\text{UO}_2$  by means of diffusion through the tungsten lattice. On cooling, the fuel, which then contains an excess of uranium atoms, reverts to  $\text{UO}_2$  with the precipitation of uranium. The large difference in the thermal



X100



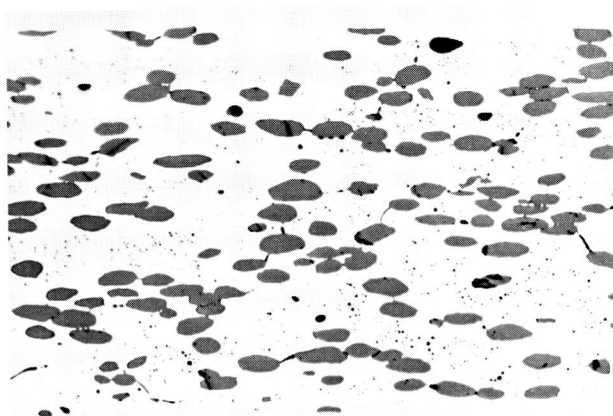
X500



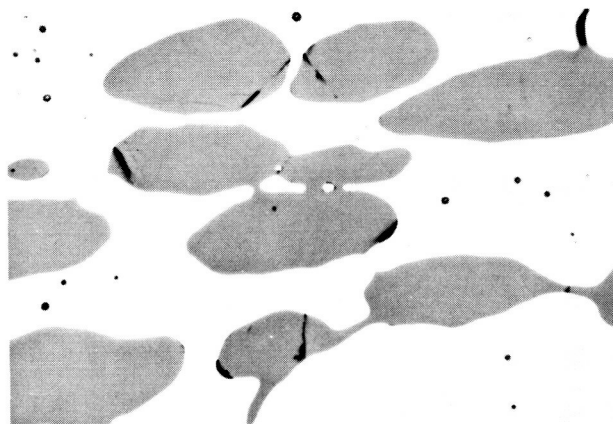
X1000

(a) Hydrogen. Five 1-hour cycles.

Figure 13. - Microstructure of thermally cycled, roll-clad 80-volume-percent-tungsten - 20-volume-percent-uranium dioxide samples. Samples were heat-treated at 4500° F with intermittent cooling to ambient temperatures in hydrogen, helium, and vacuum. Unetched.

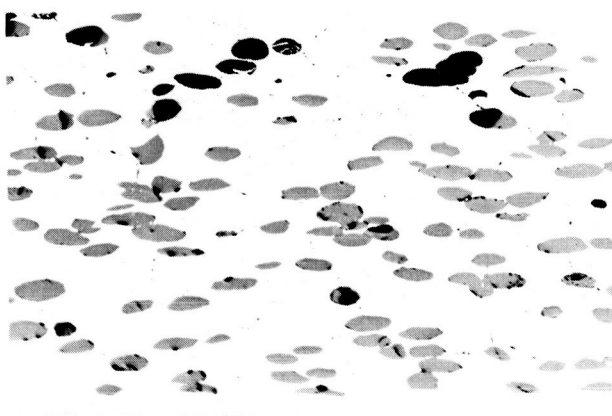


X100



X500

(b) Helium. Fifteen 1-hour cycles.



X100



X500

(c) Vacuum. Eight 1-hour cycles.

Figure 13. - Concluded. Microstructure of thermally cycled, roll-clad 80-volume-percent-tungsten - 20-volume-percent-uranium dioxide samples. Samples were heat-treated at 4500° F with intermittent cooling to ambient temperatures in hydrogen, helium, and vacuum. Unetched.

expansivities of tungsten, uranium dioxide, and uranium (refs. 9 and 10) provides a force to drive the uranium-rich phase into the tungsten grain boundaries during subsequent thermal cycling. The presence of a hydrogen atmosphere apparently accelerates the decomposition of the  $UO_2$  by combining with the oxygen being released at elevated temperatures and thereby creates a greater supply of uranium. Apparently, a vacuum also promotes decomposition of the  $UO_2$  probably by allowing the removal of oxygen atoms from the tungsten matrix.

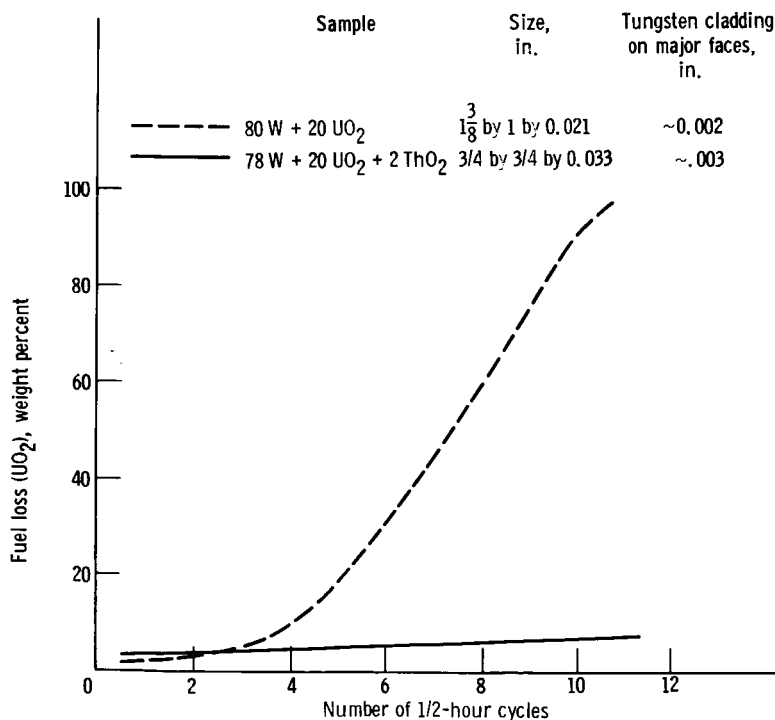
#### Methods of Inhibiting Thermal-Cycling-Induced Fuel Migration

In the studies concerned with the effects of sample variables on fuel migration during thermal cycling, preliminary results have been obtained for the variables of fuel particle size and stabilizing additives. Several roll-clad 80W + 20  $UO_2$  samples containing an average fuel particle size of 3 microns in diameter (as compared with 50- $\mu$  diam. samples) were subjected to a series of





Figure 14. - Microstructure of thermally cycled roll-clad 80-volume-percent-tungsten - 20-volume-percent-uranium dioxide sample with 3-micron average size uranium dioxide particles. Sample was heat-treated for five 2-hour intervals at 4500° F in hydrogen with intermittent cooling to ambient temperatures. Unetched. X500.



five subsequent 2-hour cycles at 4500° F in hydrogen. These samples lost fuel at a relatively low constant rate, and very slight evidence of fuel migration was observed in subsequent metallographic examinations of the samples, as shown in figure 14. The effect of fuel particle size is readily apparent when the microstructure of figure 14 is compared with that shown in figure 10(c), in which the average fuel particle diameter is 50 microns.

Figure 15. - Effect of thermal cycling roll-clad 78-volume-percent-tungsten - 20-volume-percent-uranium dioxide - 2-volume-percent-thoria sample. Sample was subjected to subsequent heat treatments at 1/2-hour intervals at 4500° F in hydrogen (35 standard cu ft/hr) with intermittent cooling to ambient temperatures.

Samples containing small amounts of thoria (ThO<sub>2</sub>) additives have

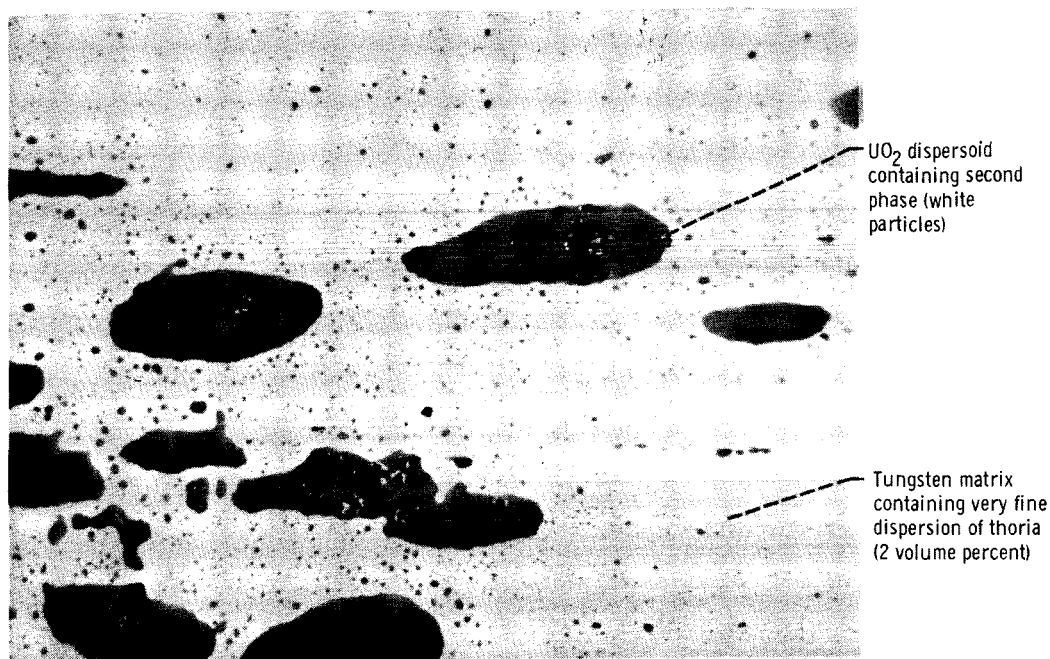


Figure 16. - Microstructure of fueled region in thermally cycled, roll-clad 78-volume-percent tungsten - 20 volume-percent uranium dioxide - 2-percent-thoria sample. Sample was heat-treated for eleven 1/2-hour intervals at 4500° F in hydrogen (35 standard cu ft/hr) with intermittent cooling to ambient temperatures. Unetched. X500.

been cycled, and some of these have not shown any evidence of fuel migration. As an example, a face-clad sample of 78W + 20UO<sub>2</sub> that had 2 volume percent thoria added to the tungsten matrix was subjected to a series of 1-hour cycles at 4500° F in hydrogen. Fuel loss data for this sample is compared with that for a face-clad 80W + 20UO<sub>2</sub> sample in figure 15. The sample containing the thoria additive exhibited a low constant fuel loss rate through 11 cycles. Subsequent metallographic examinations at high magnifications (up to X1000) showed no evidence of fuel migration in this thoriated sample. A photomicrograph of the cross section of this cycled sample is shown in figure 16. This photomicrograph indicates that no fuel migration occurred during cycling even though an additional phase (probably uranium metal) was present in the UO<sub>2</sub> particles.

### CONCLUSIONS

The following conclusions were drawn from a study of fuel-retention properties of tungsten - uranium dioxide composites during continuous and cyclic heat treatments to 4500° F:

1. Several feasible approaches to obtaining tolerable levels of fuel loss have been shown to be effective during continuous heat treatments. One method requires the fuel element to be completely encapsulated in tungsten, and the following processes have shown considerable promise for this use:

- [REDACTED]
- a. Gas-pressure bonding
  - b. Vapor decomposition
  - c. Plasma spraying

2. Coating of individual fuel particles prior to consolidation into dense bodies has also shown promise as a method of minimizing fuel loss during continuous heat treatments.

3. Migration of the fuel is predominantly dependent on thermal cycling as opposed to continuous heat treatments.

4. The number of thermal cycles has a more pronounced effect in producing the initial fuel migration than does total time at temperature.

5. Thermal-cycling atmospheres can have variable effects:

- a. Helium - no appreciable effect on fuel migration
- b. Vacuum - slight acceleration of fuel migration
- c. Hydrogen - great acceleration of fuel migration

6. The extent of fuel migration during cyclic heat treatments may depend on the size of the fuel particles with superiority shown for fine fuel particles.

7. Thoria additions to the tungsten matrix greatly reduce migration of the fuel during cyclic heat treatments.

Although the results of the thermal-cycling studies are preliminary, it is believed that the thermal-cycling problem can be solved mainly through the use of metal oxide additions, such as thoria, to the tungsten-uranium dioxide composites. The use of these additions in conjunction with the cladding approach should enhance the fuel retention properties of the tungsten - uranium dioxide composites.

Lewis Research Center  
National Aeronautics and Space Administration  
Cleveland, Ohio, September 29, 1964

#### REFERENCES

1. Lietzke, A. F.: NASA - Lewis Research Center Concept of the Nuclear Rocket Engine. Paper Presented at Materials Information Meeting, Argonne Nat. Lab., Mar. 1964.

- [REDACTED]
2. Saunders, N. T., Watson, G. K., and Buzzard, R. J.: Investigation of Tungsten and Uranium Dioxide as a Nuclear Rocket Fuel Material. Proc. Nuclear Prop. Conf., Monterey (Calif.), TID 7653 pt. II, book 2, 1962, pp. 454-462.
  3. Watson, G. K., and Buzzard, R. J.: Fabrication and Mechanical Properties of Tungsten -  $\text{UO}_2$  Composites. Paper Presented at Materials Information Meeting, Argonne Nat. Lab., Mar. 1964.
  4. Katz, J. J., and Rabinowitch, E.: The Chemistry of Uranium. McGraw-Hill Book Company, Inc., 1951, p. 262.
  5. Grisaffe, Salvatore J., and Caves, Robert M.: Fuel Retention Improvement at High Temperatures in Tungsten - Uranium Dioxide Dispersion Fuel Elements by Plasma-Spray Cladding. NASA TM X-1028, 1964.
  6. Rothwell, E.: High Temperature Substoichiometry in Uranium Dioxide. Jour. Nuclear Materials, vol. 6, no. 2, July 1962, pp. 229-236.
  7. Gripshover, P.: Fabrication of Core Structures. Paper Presented at Materials Information Meeting, Argonne Nat. Lab., Mar. 1964.
  8. Powell, C. F., Campbell, I. E., and Gonser, B. W.: Vapor-Plating. John Wiley & Sons, Inc., 1955, pp. 1-23; 55-58.
  9. Staff of Nuclear Materials and Propulsion Operation: High-Temperature Materials Program. Prog. Rep. 17, pt. B, GEMP-17B, General Electric Co., Nov. 15, 1962, p. 23.
  10. Tipton, C. R., Jr., ed.: Reactor Handbook. Vol. I. Materials. Second ed., Interscience Pub., Inc., 1960, pp. 117-119.